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Polymerization of Blocked Isocyanate Functional Polymer Surfaces and Post-Polymerization Modification By Thiol-Isocyanate Reactions

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The University of Southern Mississippi

POLYMERIZATION OF BLOCKED ISOCYANATE FUNCTIONAL POLYMER
SURFACES AND POST-POLYMERIZATION MODIFICATION BY THIOL-
ISOCYANATE REACTIONS

by

Chase A. Tretbar

A Thesis
Submitted to the Honors College of
The University of Southern Mississippi
in Partial Fulfillment
of the Requirements for the Degree of
Bachelor of Science
in the Department of Polymer Science and High Performance Materials

May 2015

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ABSTRACT

Direct polymerization of isocyanate-functional monomers has been achieved with controlled radical polymerizations (CRP) for precisely engineered modification platforms with highly reactive side chains. However, despite the success of these strategies, the inherent reactivity of isocyanates still leads to adverse side reactions, such as hydrolysis, that are difficult to suppress. Phenol, lactam, and oxime-based blocking agents have been used to limit the reactivity of isocyanates in applications such as multicomponent urethane coating systems. The reactivity of these blocked isocyanates can be restored by thermal deprotection of the blocking agent to achieve the desired reactions. In this work, we use blocked isocyanate-functional monomers for surface-initiated polymerization. The isocyanate functional group allows facile modification of the side chains by thiol-isocyanate "click" reactions, while the blocking agent reduces detrimental side reactions like hydrolysis. We investigate thermally labile blocking agents and report the synthesis and characterization of the blocked isocyanate-functional polymers, followed by deprotection and modification of the isocyanates by reaction with thiols.

Key Terms: polymer, isocyanate, thiol, surface, click, brush

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LIST OF ABBREVIATIONS

SIP – Surface initiated polymerization

PPM – Post polymerization modification

NCO – Isocyanate

SAMs- Self-Assembled Monolayers

MW – Molecular Weight

EWG – Electron Withdrawing Group

REO – Robust, Efficient, Orthogonal

DBU – 1,8-diazabicyclo[5.4.0] undec-7-ene

NMR – Nuclear Magnetic Resonance

gATR-FTIR – Grazing Angle Attenuated Total Reflectance Fourier Transform

Infrared Spectroscopy

CHAPTER I:

INTRODUCTION

Applications for advanced functional materials that possess precisely engineered surface properties are expanding rapidly with the development of nanotechnology and the ever growing need to address resource, health, and energy issues. Demand is increasing the necessity to fabricate soft material surfaces with precise control over architecture, domain size, functionality, polarity, and reactivity for an array of applications including antifouling coatings, biosensors, photovoltaics, and tissue engineered scaffolds.

This broad range of requirements necessitates the development of a modular approach to surface engineering – ideally one that (1) enables the rapid generation of a diverse library of functional surfaces from a single substrate precursor, (2) utilizes a structurally diverse range of commercially available or easily attainable reagents, (3) proceeds rapidly to quantitative conversions under mild conditions and (4) opens the door to orthogonal and site-selective functionalization. Recent advances in synthetic polymer chemistry have resulted in numerous fundamental scientific discoveries that enable the development of materials and surfaces with attributes such as those described above.¹

Among different techniques of functional surface engineering, the combination of surface-initiated polymerization (SIP) and post-polymerization modification (PPM) offers unique advantages.² Surface-initiated polymerization opens the door to highly controlled polymer structures on the surface from a variety of commercially available monomers. Post-polymerization modification, on the other hand, is based on the direct polymerization of monomers bearing chemoselective handles that are inert towards the

polymerization conditions, but can be quantitatively converted to a broad range of functional groups in a subsequent step.³ PPM enables one to take full advantage of the versatility of the SIP technique while extending the range of functional groups that can be bestowed to the surface.

This thesis leverages “thiol-click” reactions – particularly the reaction between a thiol and an isocyanate (NCO) - in combination with SIP to design and fabricate surfaces with facile, efficient routes to functionalization. Given that isocyanates are highly reactive and inherently moisture sensitive, this work focuses specifically on the reaction of protected, or blocked NCOs with thiol functional groups via an addition-elimination route for post-modification of polymer brush surfaces. As illustrated in Figure 1, the overarching goal of this prospectus is to elucidate the appropriate design of blocked NCOs and the most favorable reaction conditions to facilitate the thiol-blocked NCO reaction at ambient temperatures for polymer surface modification. The stated goal will be pursued via exploration of the following research objectives:

1. Synthesis of model blocked isocyanate compounds comprising imidazole, pyrazole, and 1,2,4-triazole as blocking agents, and reaction of these model compounds with thiols at ambient temperature to elucidate structure-reactivity relationships via kinetic analysis.
2. Synthesis of polymer brush surfaces with pendent blocked-NCO functional groups via surface-initiated photopolymerization. The moisture and temperature stability of these surface will be evaluated.
3. Post-polymerization modification of blocked-NCO polymer brush surfaces with thiols using reaction conditions identified in objective 1.

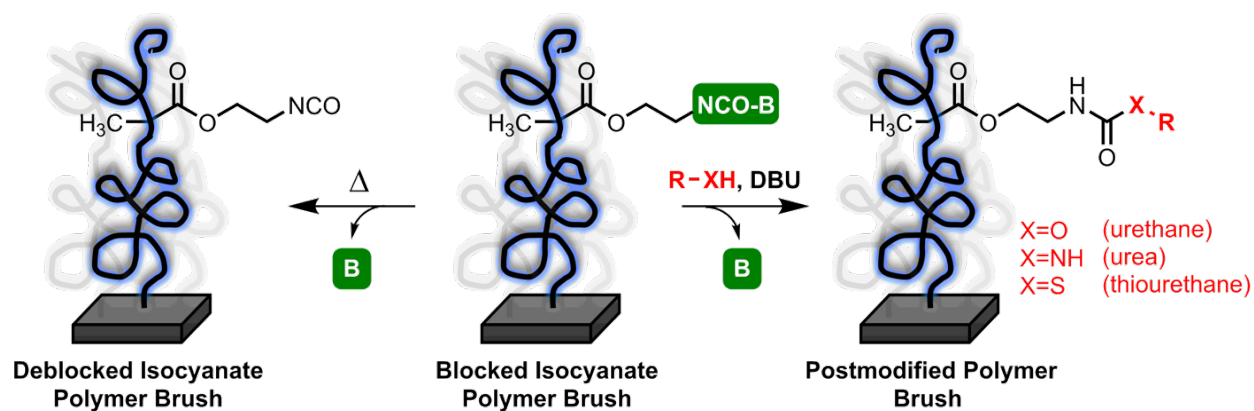


Figure 1 - Schematic representation of the postpolymerization modification process on blocked isocyanate polymer brush surfaces. The green “B” group represents an imidazole, pyrazole, or triazole blocking agent. The thermally reversible regeneration of the reactive isocyanate is shown by the left arrow process, while the base-catalyzed addition-elimination reaction between the blocked-NCO and thiol is shown by the right arrow process.

CHAPTER II:

LITERATURE REVIEW

Surface-Initiated Polymerization

Surface-initiated polymerization (SIP) represents one of the most effective and versatile methods for tailoring the physio-chemical properties of surfaces.⁴ SIP offers a direct means to control the density, thickness, and functionality of ultrathin films by growing polymer chains directly from surface bound initiators. At high grafting, the macromolecules adopt a highly stretched conformation extending perpendicular to the substrate surface in order to avoid chain overlap, or the so-called “polymer brush” conformation.⁵ The ability to conformally modify substrates of any geometry with outstanding film homogeneity at nanometer thicknesses offers many advantages over solution cast films. Additionally, the three-dimensional brush conformation of SIP brushes greatly enhances the functionality of the surface by providing not only an opportunity to present functional groups at the interface, but also throughout the film – as each monomer unit is capable of carrying a functional moiety.⁶ This feature makes SIP vastly superior to self-assembled monolayers (SAMs) where functionality is limited to the outermost edge of the interface. The ability to endow a surface with 3D functionality has tremendous advantages for applications where high functional group densities are required, e.g. membranes and biosensor chips.⁷ When properly designed, polymer films fabricated by SIP are stable under a variety of environmental conditions owing to the covalent interaction of the polymer chains with the substrate surface.

Post-Polymerization Surface Modification

Despite recent advances in the SIP approach, there remains a large number of pendent functional groups that cannot be directly polymerized from the surface due to i) steep cost of functional monomer synthesis, ii) intolerance of the functional moiety in the polymerization process (i.e. reactivity, steric bulk), and iii) instability of the pendent functional group following polymerization (i.e. hydrolysis, oxidation, etc.). This often necessitates the development of a modular approach to surface engineering in the form of post-polymerization modification (PPM) (i.e. transformation of reactive functional groups following the polymerization process). PPM of polymer surfaces, when combined with SIP, has evolved as a powerful approach to engineer polymer surfaces with complex functionality.⁸⁻¹⁰ PPM circumvents limitations associated with direct polymerization of functional monomers due to intolerance of many functional groups with the polymerization mechanism and/or reaction conditions (i.e. reactivity, steric hindrance, temperature/light sensitivity).¹¹ PPM of reactive polymer surfaces in the brush regime – where polymer chains are densely grafted to a surface such that the polymer chains overlap, experience strong segmental repulsion and accordingly stretch perpendicular to the surface^{5, 12} – is particularly challenging. The stretching of the tethered chains reduces chain conformational entropy rendering the penetration of the brush by reactive modifiers from solution highly unfavorable. Thus, the efficiency, depth of penetration, and homogeneity of the PPM process in the brush regime are ultimately dependent on parameters associated with i) the reaction conditions (i.e. reaction efficiency, solvent quality) ii) the tethered polymer brush (i.e. grafting density and thickness) and iii) the physical properties of the unbound, reactive modifier (i.e. molecular weight (MW), steric

bulk). Thus, PPM of polymer brush surfaces necessitates the use of reactions with high reactivity and efficacy – such as those reactions described as “click” reactions (*vide infra*). Presently, a broad range of chemical and biological moieties have been installed on brush surfaces via the PPM “click” methodologies providing surfaces for catalysis,^{13, 14} separations,¹⁵ controlled release,¹⁶ patterning,¹⁷⁻²⁰ barrier properties,²¹ and biological activity.²²⁻²⁴

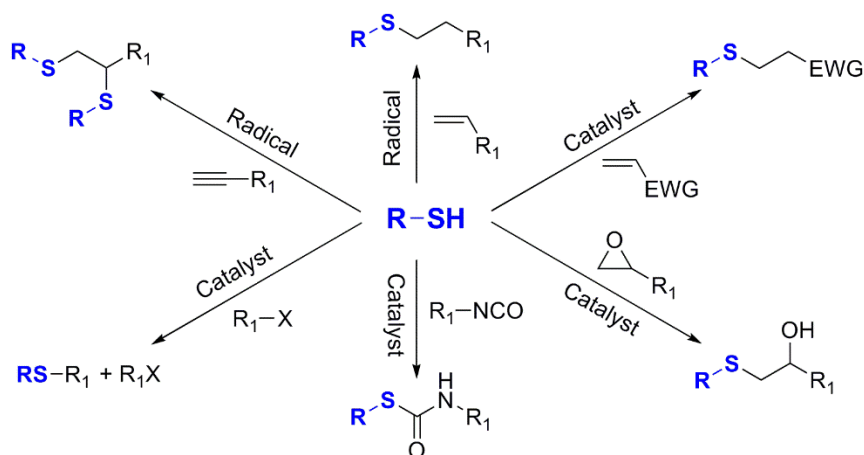


Figure 2 - Toolbox of thiol-click reactions. EWG = electron withdrawing groups; X = Br, Cl and R₁ = aliphatic or aromatic groups.

Thiol-Click Reactions

“Click” chemistries are known as “Robust, Efficient, Orthogonal” (REO) strategies to tailor-make polymeric materials with specific function. Among different “click” reactions, thiol-click reactions have emerged as valuable tools for the synthetic polymer chemist. Specifically, electron rich alkenes (radical), alkynes (radical), electron poor alkenes (Michael addition), isocyanates (carbonyl addition), epoxies (S_N2 ring opening), and halogens²⁵⁻²⁷ (S_N2 nucleophilic substitution) all readily react with thiols,

thus comprising a *toolbox* of efficient chemical reactions as depicted in Figure 2.²⁸ Recently, we and others have shown thiol-based click reactions – such as thiol-ene²⁹⁻³³, thiol-yne^{17, 32, 34-37}, and thiol-isocyanate^{38, 39} – to be a powerful approach for engineering multifunctional materials and surfaces in a modular fashion. These reactions proceed at room temperature with high efficiency and rapid kinetics, in the presence of oxygen/water, without expensive and potentially toxic catalysts, and are highly tolerant of a wide range of functional groups. The wide commercial availability of thiols as well as the rapid reaction kinetics of the base-catalyzed thiol–isocyanate reaction (using 1,8-diazabicyclo[5.4.0] undec-7-ene (DBU) as the base) makes this reaction extremely attractive towards the fabrication of highly functional surfaces. Importantly, this chemistry lacks the need for protection of the clickable moiety during surface-initiated photopolymerization. However, the sensitivity of the isocyanate function group to water under ambient conditions limits the stability of the brush surfaces upon storage. The use of protected isocyanate groups that are stable under ambient conditions, but undergo rapid and reversible deprotection or direct displacement reactions with thiols would present an ideal platform for PPM of brush surface. The concept of blocked isocyanates is discussed in the next section and represents the crux of this research prospectus.

Blocked Isocyanates

Isocyanates are highly reactive, inherently sensitive to water, and undergo rapid hydrolysis under ambient conditions if no precautions (i.e. dry nitrogen atmosphere) are implemented (Figure 3a). In an unprotected form, isocyanates readily react with alcohols, amines and thiols to form urethane, urea, and thiourethane linkages, respectively, as shown in Figure 3a. Collectively, these reactions underpin many

industrial technologies such as polyurethane coatings, foams, and thermoplastic elastomers. The isocyanate functional group can be protected, or “blocked”, by reacting the isocyanate with an active hydrogen compound such as phenols, ketoximes, amides, and nitrogen heterocycles (i.e. imidazole,⁴⁰ pyrazole⁴¹).⁴² In a typical application, blocked isocyanates are exposed to heat and undergo an elimination reaction to regenerate the reactive isocyanate and the active hydrogen compound. In the presence of a nucleophile (i.e. alcohols, amines and thiols), the regenerated isocyanate can proceed as previously described to form urethane, urea, and thiourethane linkages. The elimination-addition blocking scheme, as shown in Figure 3a, has been used in coatings applications for shelf-stable formulations that can be activated at elevated temperatures; however, relatively high temperatures (100 – 200 °C) are often necessary to facilitate the deblocking reaction which can limit the applicability of blocked NCOs for certain applications. The deblocking temperature depends on the structure of both the isocyanate and the blocking compound. An alternate scheme to utilize blocked NCOs is shown in Figure 3b. In the addition-elimination route, the nucleophile reacts directly with the blocked NCO to yield a tetrahedral intermediate followed by elimination of the blocking agent.

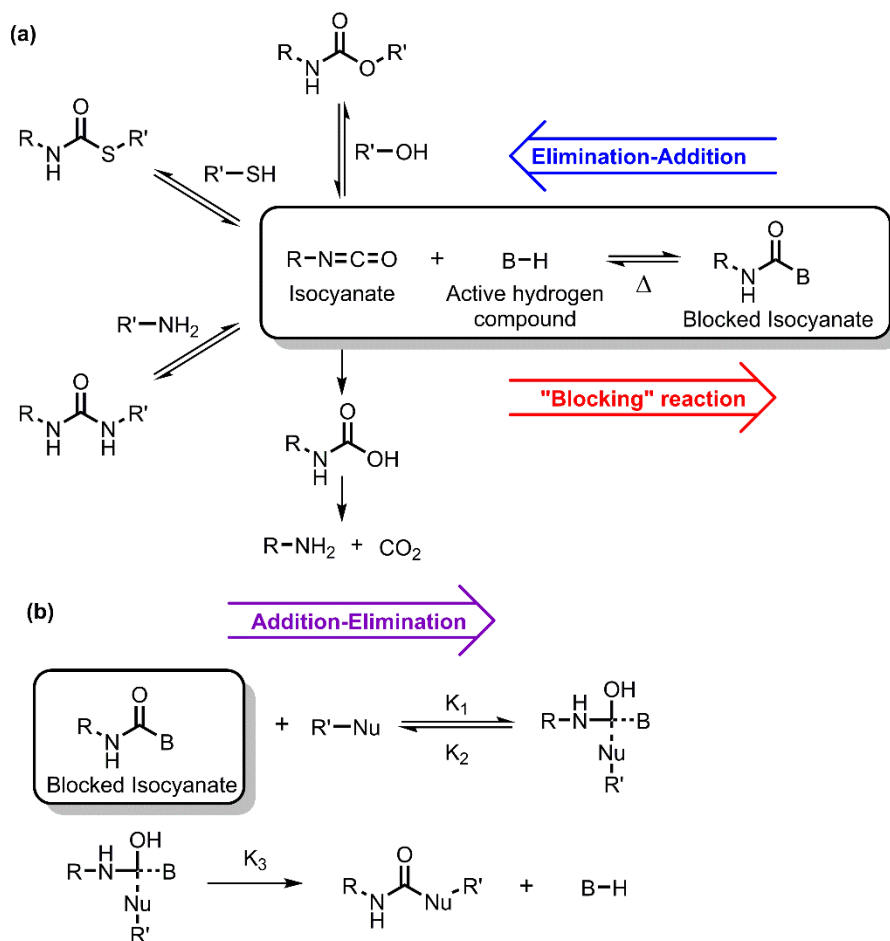


Figure 3 - (a) Scheme illustrating the blocking reaction of isocyanates and the elimination-addition reaction of blocked isocyanates at elevated temperatures. The regenerated NCO group can readily react with various nucleophiles (alcohol, amines, thiols, water). (b) The addition-elimination route available by reaction of a nucleophile directly with a blocked isocyanate.

While blocked NCOs have been widely used at elevated temperatures for crosslinking reactions in coatings applications⁴³ (with contributions from both the elimination-addition and addition-elimination mechanisms), the exploration of blocked isocyanates as a postpolymerization modification approach has scarcely been reported. A recent example by Bode et al.⁴⁴ demonstrated the use of blocked isocyanates for post-

polymerization end group modification of α,ω -telechelics (prepared by reversible addition-fragmentation chain transfer polymerization) via reaction of the blocked NCO end groups with small molecule amines and alcohols at elevated temperatures (130 °C). The addition-elimination scheme at ambient temperature has received minimal attention as a route to functional materials and surfaces. The few examples reported in the peer-reviewed literature have only focused on the reaction of primary amines with blocked NCOs under ambient conditions.⁴⁵⁻⁴⁷ To our knowledge, the reaction of thiols directly with blocked NCOs under ambient conditions has not been reported.

CHAPTER III:

EXPERIMENTAL METHODS

Surface characterization of polymer brushes can be somewhat of a challenge. Because of their reduced dimensionality, assumptions based on analogous solution or bulk systems do not necessarily hold. Indeed, other than synthesis, a large part of the success in investigating polymer brushes is proving their dimensionality and that the physical and chemical properties of polymers are unique when tethered to surfaces. By focusing on surface-initiated polymerizations on flat ideal surfaces, it is possible to take advantage of a wide variety of surface-sensitive spectroscopic, microscopic, and optical techniques.

Techniques for determining the chemical functional group and molecular (elemental) species on synthesized polymer brushes include grazing angle Fourier transform infrared spectroscopy (gATR-FTIR) and ellipsometry. Grazing angle-FTIR will allow monitoring specific IR-sensitive functional groups, even at monolayer thicknesses. This technique allows for functional group monitoring starting with surface initiator functionalization to polymer brush formation and modification. Particularly, chemical group identification or disappearance of post-polymerization modified polymer brushes that have undergone chemical conversion will be assessed. Grazing angle-FTIR will be particularly useful in determining the complete disappearance blocking agents and appearance of thiocarbamate or isocyanate moieties as the blocking agents are removed.

This method can also be used to determine the thermal regeneration of the isocyanate from the blocking agent.

Ellipsometry has been used widely and routinely to investigate film thickness of polymer brushes and was used to determine initiator monolayer thicknesses as well as polymer brush thickness. Ellipsometry measures a beam of polarized light that is reflected off of silicon surfaces. The change in refractive index from the standard can be correlated back to the surface thickness. Ellipsometry was performed before and after deprotection and functionalization through thiol-click reactions.

Water contact angle (WCA) measurements provided by a contact angle goniometer will allow for the determination of surface energy or surface tension which is dependent on the hydrophobicity or hydrophilicity of the functional moieties incorporated into the polymer brush. Static water contact angles will confirm the expected changes in wettability associated with each functional moiety conjugated to the surface.

Materials

All reagents, unless otherwise stated, were obtained at the highest purity available from Sigma Aldrich Chemical Company and used without further purification. The pyrazole-blocked isocyanate methacrylate (KarenzMOI-BPTM) was obtained from Showa-Denko, Inc. (Japan), and passed through a neutral alumina plug to remove inhibitor. 2-isocyanatoethyl methacrylate was obtained from TCI Chemicals. Wako Pure Chemicals, Ltd. was supplied for the low temperature initiator, V-70.

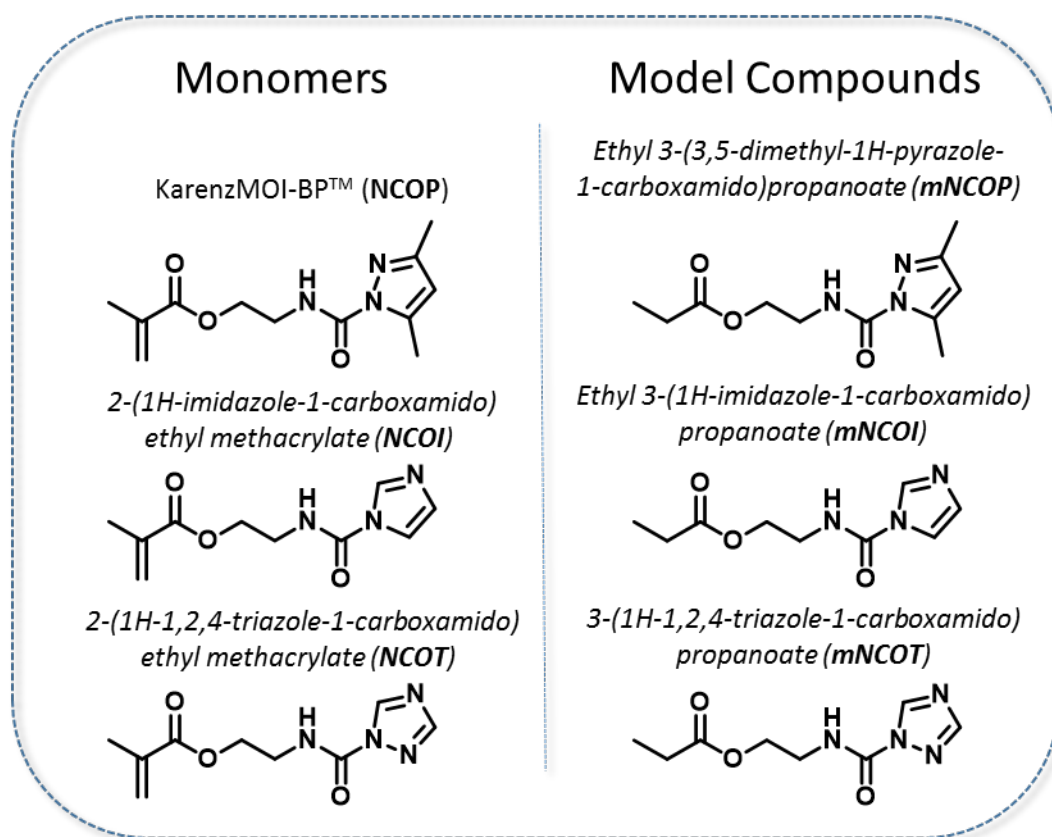


Figure 4 - Chemical structures for blocked-NCO monomers.

Synthesis

Synthesis of *Ethyl 3-(3,5-dimethyl-1H-pyrazole-1-carboxamido)propanoate (mNCOP)*:

Ethyl-3-isocyanatopropionate (1.49 g, 10.4 mmol) was added dropwise over 15 minutes to a stirred solution of pyrazole (1 g, 10.4 mmol) in a 1:1 molar ratio in ether (50 mL).

The reaction was allowed to run for an hour at room temperature. The product was isolated from ether by rotary evaporation and re-dissolved in CH₂Cl₂. The product was then transferred to a separatory funnel and washed separately with both 150 mL of deionized water and brine solution, respectively. The organic layer was dried over

MgSO₄, filtered, and the solvent was removed by rotary evaporation and high vacuum to give a colorless oil (2.05 g, 82.4% yield).

Synthesis of 2-(*1H*-imidazole-1-carboxamido)ethyl methacrylate (NCOI):

2-Isocyanatoethyl methacrylate (7.30 g, 47.0 mmol) was added dropwise over 15 minutes to a stirred solution of imidazole (3.20 g, 47.0 mmol) in a 1:1 molar ratio in ether (100 mL). The reaction was allowed to proceed for an hour during which the product precipitates as a white solid. Upon reaction completion, the white solid was filtered and dried under vacuum to give a yield of 9.94 g (95% yield).

Synthesis of Ethyl 3-(*1H*-imidazole-1-carboxamido)propanoate (mNCOI):

Ethyl-3-isocyanatopropionate (1.93 g, 13.5 mmol) was added drop wise to a stirred solution of imidazole (0.917 g, 13.5 mmol) in ether (50 mL) over 10 minutes. The reaction was stirred for an hour at room temperature, while a white precipitate formed. After completion of the reaction, the solid precipitate was filtered, washed with ether, and dried under vacuum to give 2.58 g (91% yield).

Synthesis of 2-(*1H*-1,2,4-triazole-1-carboxamido)ethyl methacrylate (NCOT):

1,2,4-triazole (4.00 g, 58.0 mmol) was first dissolved in a solution consisting of 4:5 (v/v) THF (80 mL) to ether (100 mL). Next, 2-Isocyanatoethyl methacrylate (9.00 g, 58.0 mmol) was added drop wise in a molar ratio of 1:1 to the 1,2,4-triazole mixture over the course of 15 minutes. The reaction was stirred for 3 hours, while the product precipitated as a white solid. After completion of the reaction, the solid precipitate was filtered, washed with a THF/ether mixture, and dried under vacuum to give 9.01 g (70% yield).

Synthesis of *3-(1H-1,2,4-triazole-1-carboxamido)propanoate (mNCOT)*:

1,2,4-triazole (0.91 g, 13.2 mmol) was first dissolved in a solution consisting of 1:2 THF (15 mL) to ether (30 mL). Next, ethyl-3-isocyanatopropionate (1.89 g, 13.2 mmol) was added dropwise in a molar ratio of 1:1 to the 1,2,4-triazole mixture over the course of 5 minutes. The reaction was stirred for 2 hours, while the product precipitated as a white solid. The product was filtered, washed in a THF/ether mixture, and dried under vacuum to give 1.62 g (58% yield).

Small molecule thiol exchange

Small molecule model reactions were performed to determine the reaction kinetics of the exchange between thiol and blocked isocyanates at room temperature. The kinetic experiments consisted of a 1:1 molar ratio of thiol to blocked isocyanates. The exchange was catalyzed by triethylamine or DBU (at 10 and 30 mol percent) to determine the effect of catalyst concentration and type. The model reactions were monitored by NMR spectroscopy. The two thiols that were used to monitor the rates were 1-hexanethiol and benzyl mercaptan as shown in Figure 5. The model blocked isocyanate was first dissolved in 1 mL deuterated DMSO to yield a 0.2 M solution. The thiol component was then added to the blocked isocyanate solution and an initial NMR spectrum was obtained. After the initial NMR scans, the catalyst was added followed immediately by another NMR run to generate the first time point for the reaction. Subsequent NMR spectra were obtained at various times to monitor the reaction conversion. The appearance and disappearance of certain peaks relative to unchanging peaks allow for the determination of reaction progress. Conversion vs. time plots were created to analyze the reaction rate.

The kinetic studies were performed for three different blocked isocyanate model compounds to determine the impact of the specific blocking agent on the rate of the reaction.

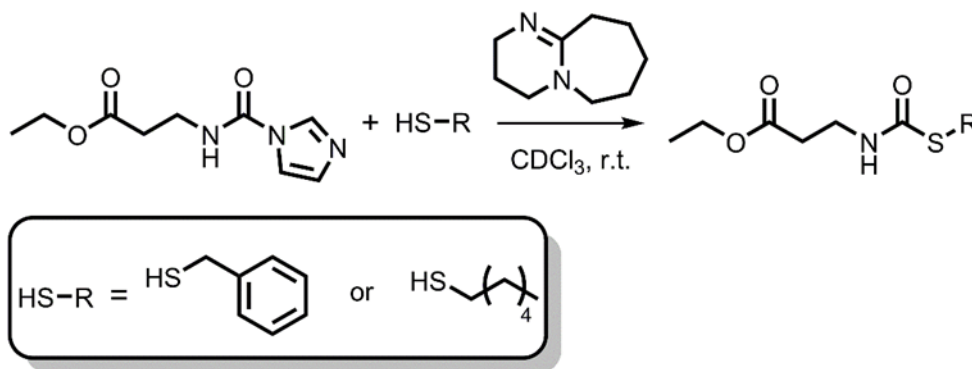


Figure 5 - Reaction between thiols and ethyl 3-(1H-imidazole-1-carboxamido)propanoate used to elucidate thiol/blocked-NCO reaction kinetics.

Surface-Initiated Photopolymerization.

Silicon wafers were cleaned and functionalized with a surface-based initiator as reported in previous literature.¹⁷ The imidazole, pyrazole, and triazole-based monomers were then individually dissolved in DMSO to create 1.0 M solutions. The monomer solutions were then degassed for 30 minutes by purging with dry N_2 . The polymerization reaction were performed in a N_2 purged glovebox to eliminate the interference of oxygen. The initiator-functionalized silicon wafers were immersed in the monomer solution and subsequently irradiated with UV light for four different time periods: 15min, 20min, 25min and 30min. The UV light used was an Omnicure 1000 Series at a wavelength of approximately 365nm. The intensity of the UV light was $70\text{mW}/\text{cm}^2$. After polymerization, substrates were thoroughly washed in DMSO, THF and toluene.

Post-polymerization Modification of Blocked-NCO Brushes with Thiols.

The polymerized substrates were submerged into tetrahydrofuran (THF), where various thiols (i.e. 1-hexanethiol, benzyl mercaptan, 1-dodecanethiol, and 1-thioglycerol) were added separately. Triethylamine and DBU were added separately to catalyze the exchange reaction at a concentration of 10mol percent relative to the concentration of thiol. The substrates were allowed to react overnight in a test tube shaker, where they were subsequently rinsed with THF and toluene to remove excess thiol and catalyst. The extent of the reaction was monitored through gATR-FTIR, while changes in water contact angle were measured using a contact angle goniometer.

Small Molecule Characterization.

All synthesized molecules described above will be characterized for chemical composition and primary macromolecular structure. Proton spectroscopy were primarily used to determine chemical composition, structure and purity. The model monomers were dissolved in deuterated DMSO and ran on a 300MHz Bruker NMR spectrometer.

Surface Characterization.

Wettability of the unmodified and modified polymer brushes were monitored by a Raméhart 200-00 Std.-Tilting B. goniometer. Static (θ_{sw}) contact angles were measured using 10 μ L water droplets in combination with DROPimage Standard software. Ellipsometric measurements were carried out using a Gaertner Scientific Corporation LSE ellipsometer with a 632.8 nm laser at 70° from the normal. Refractive index values of 3.86, 1.45, 1.43 and 1.5 for silicon, oxide layer, photoinitiator monolayer and all polymer layers, respectively, were used to build the layer model and calculate layer thicknesses.^{27, 28}

The chemical nature of the polymer brush surfaces was characterized by Fourier transform infrared spectroscopy (FTIR) in grazing-angle attenuated total reflectance mode (gATR-FTIR) using a ThermoScientific FTIR instrument (Nicolet 8700) equipped with a VariGATR™ accessory (grazing angle 65°, germanium crystal; Harrick Scientific). Spectra were collected with a resolution of 4 cm⁻¹ by accumulating a minimum of 128 scans per sample. All spectra were collected while purging the VariGATR™ attachment and FTIR instrument with N₂ gas along the infrared beam path to minimize the peaks corresponding to atmospheric moisture and CO₂. Spectra were analyzed and processed using Omnic software.

Chapter IV:

Results

Synthesis of Blocked Isocyanate Monomers

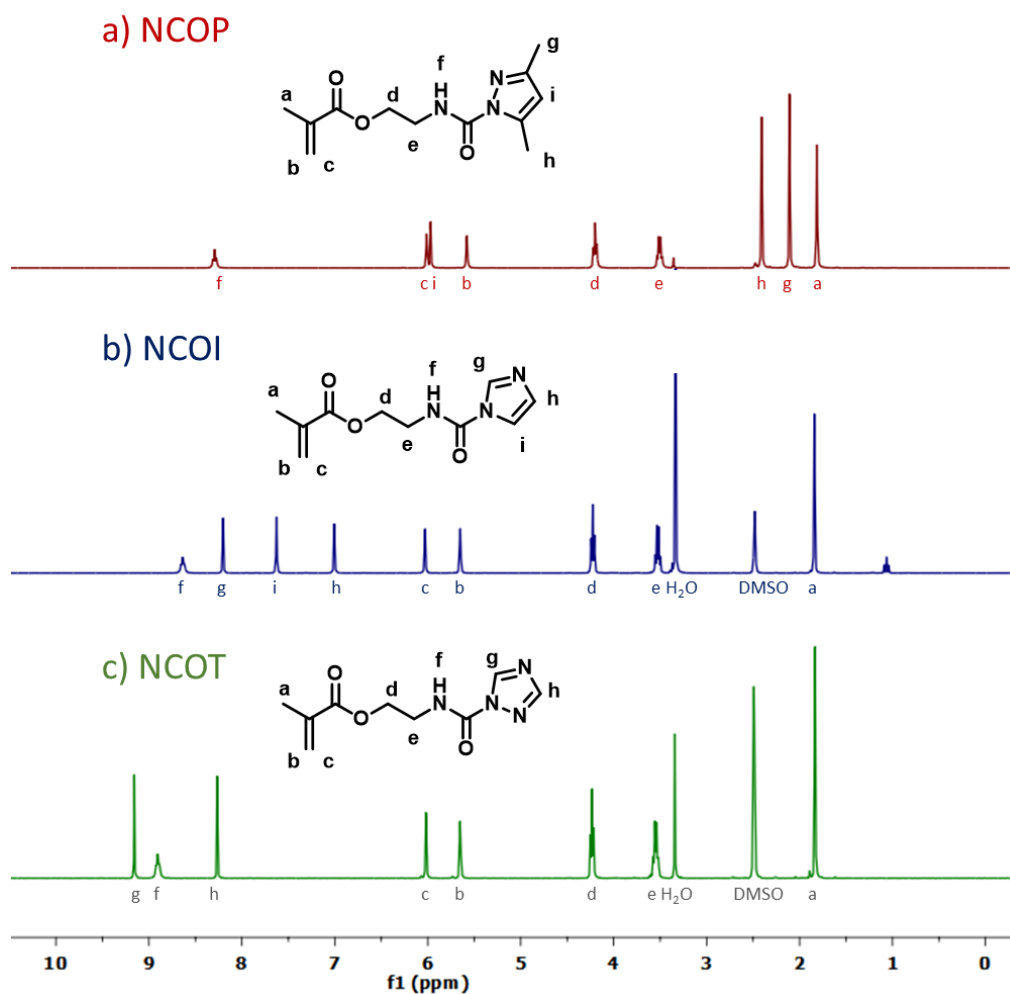


Figure 6 – NMR spectrum of a) NCOP, b) NCOI, and c) NCOT.

A series of blocked-isocyanato ethyl methacrylate monomers with a range of deblocking temperatures were either synthesized or obtained commercially. The blocking groups were varied to investigate their deblocking conditions at room temperature via

nucleophilic displacement of the blocking agent with a thiol. Imidazole-protected and triazole-protected isocyanate monomers were synthesized successfully and in high yield through a facile synthesis route. The pyrazole-protected isocyanate monomer was obtained commercially from Showa-Denko, Inc. The NMR spectra for the all of the protected isocyanate monomers are shown in Figure 6. The NMR spectra indicate that these monomers can be obtained in high purity. In figure 6a, peaks g, h, and I correspond to the pyrazole blocking agent. In Figure 6b, peaks g, h, and i correspond to the imidazole blocking agent. In Figure 6c, peaks g and h correspond to the triazole blocking agent.

Synthesis of Blocked Isocyanate Model Compounds

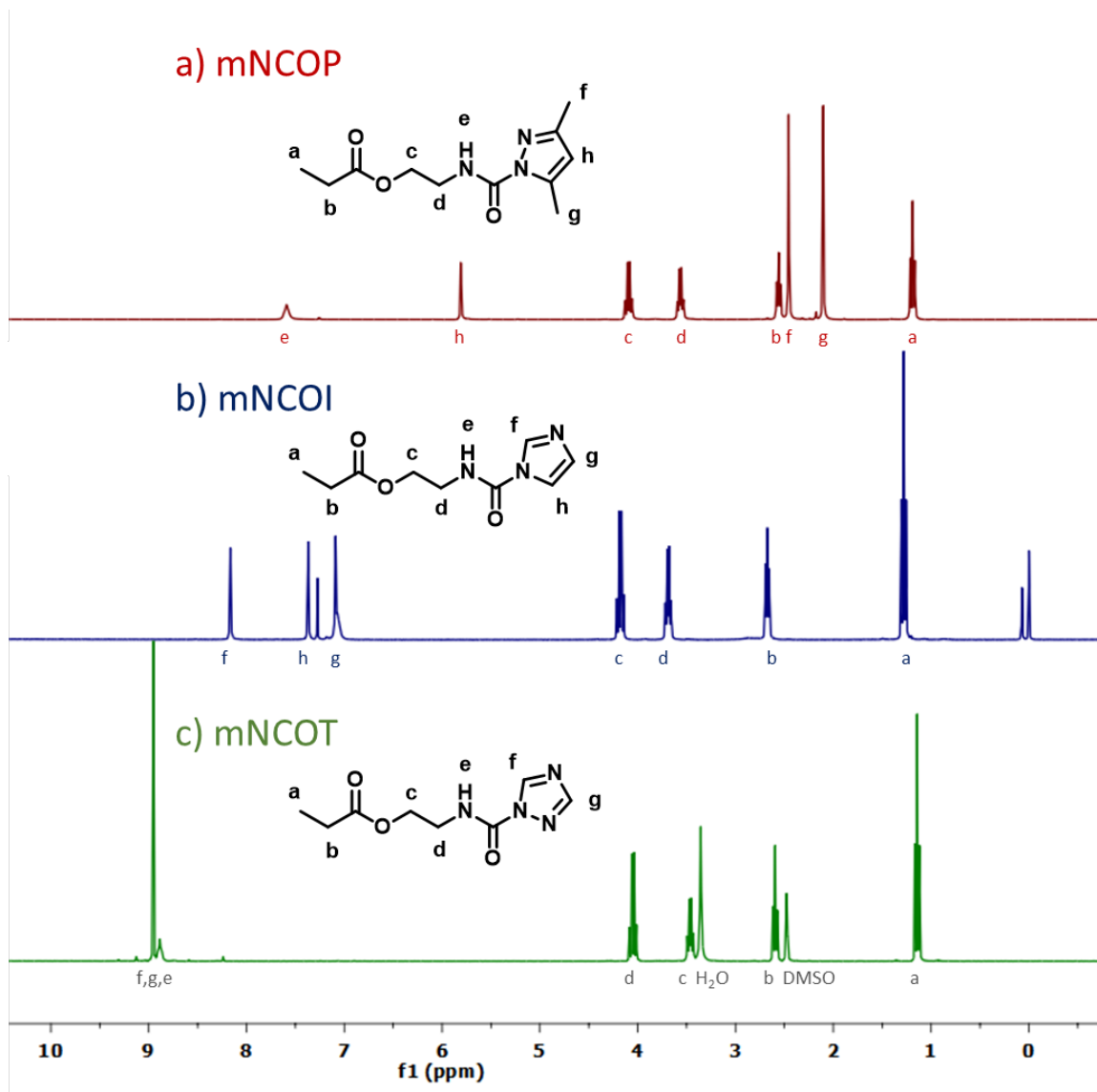


Figure 7 – NMR spectrum of a) mNCOP, b) mNCOI and c) mNCOT.

Small molecule analogs of the blocked isocyanate monomers, lacking the reactive double bonds found in the monomers, were synthesized. The model compounds were used to monitor the exchange reaction between the blocking agent and thiols at room temperature in the presence of base catalyst in order to easily determine the time scales

and conditions for these reactions. Model blocked isocyanates were used instead of the blocked isocyanate monomers for these model reactions due to the possibility of Michael addition between the acrylate groups in the monomers and the thiol anions. The small molecule compounds were synthesized in high purity and the NMR spectra for all of the molecules can be found in Figure 7. In Figure 7a, peaks f, g and h correspond to the pyrazole blocking agent. In Figure 7b, peaks f, g and h correspond to the imidazole blocking agent, while in Figure 7c, peaks f and g correlate to the triazole blocking agent.

Model Blocked Isocyanate Reactions

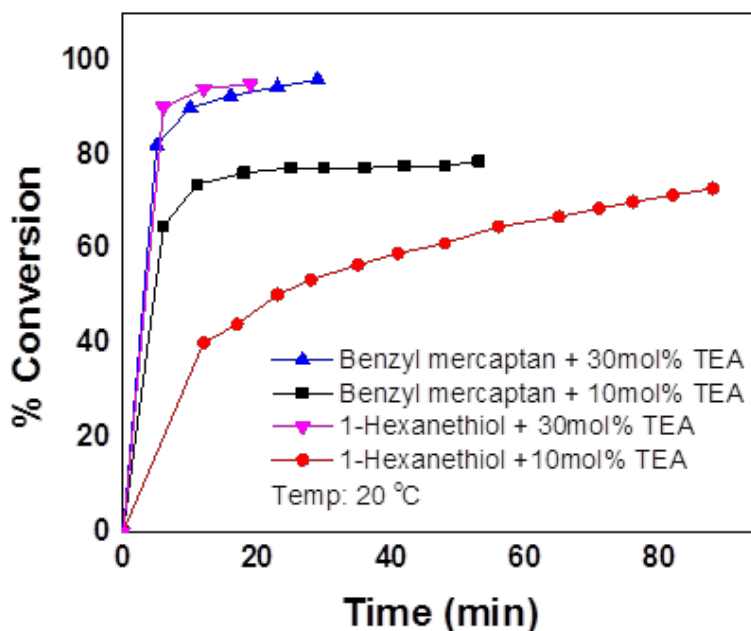


Figure 8 – Conversion vs. time plot of thiol exchange with NCOT and TEA as catalyst.

The exchange between the model blocked isocyanates and various thiols were monitored to determine the deblocking conditions for the different blocking agents via direct nucleophilic displacement. The percent conversion of the blocking agents to

thiocarbamate linkages was determined by ^1H NMR spectroscopy and plotted versus time in order to study the efficiency of the reactions. Conversion was measured by comparing the integrations ^1H NMR peaks unaffected by the model reactions with the integrations of those peaks in that shift as the reaction progresses. Figure 8 shows the calculated conversions with time for the exchange mNCOT with benzyl mercaptan and 1-hexane thiol in the presence of both 10 mol% and 30 mol% triethylamine (TEA) catalyst. At 10 mol% TEA, benzyl mercaptan rapidly proceeds to 75% conversion, and at 10 mol% TEA, 1-hexane thiol approaches 70% conversion after almost three hours. At 30 mol% TEA, the reactions with both benzyl mercaptan and 1-hexanethiol reach nearly 100% conversion after about 20 minutes.

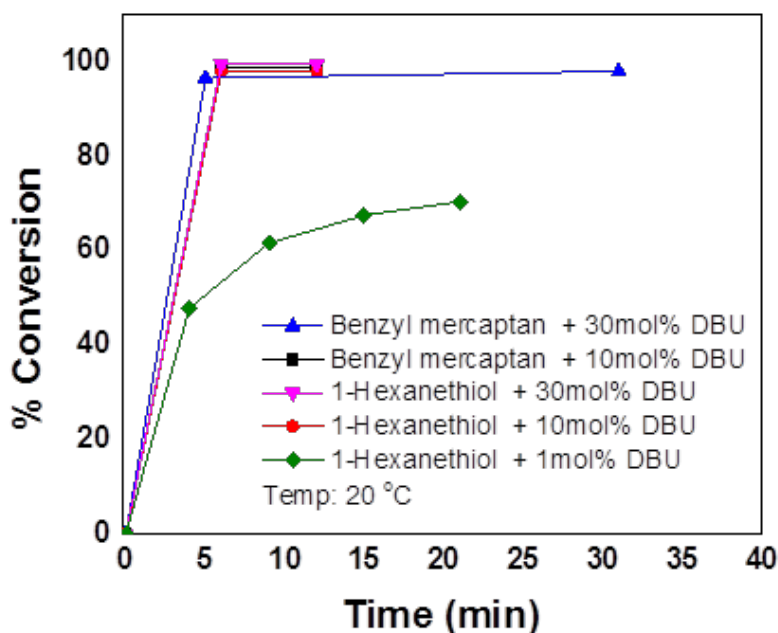


Figure 9 – Conversion vs. time plot with mNCOT and DBU as catalyst.

In Figure 9, we can see that 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) provides very rapid catalysis of the thiol-isocyanate reactions when compared to the same mole percentages of TEA. For both 1-hexanethiol and benzyl mercaptan, nearly 100% exchange took place within the first five minutes. At 1 mol% DBU, the conversion of blocked isocyanate to thiocarbamate is more gradual and only reaches about 70% conversion after 20 minutes. Future studies will investigate the interplay between heat and catalyst amounts to determine if there are intermediate conditions that lead to efficient deblocking reactions at mild temperatures and low catalyst amounts.

Polymerization of Blocked Isocyanates

The blocked isocyanate monomers (NCOP, NCOI and NCOT) were polymerized from the surface of silicon wafers through surface initiated polymerization (SIP). A surface-bound photoinitiator was used to initiate the reaction in the presence of UV light. The silicon wafer was placed into the monomer solution and subsequently subjected to UV light. The polymerization was allowed to proceed until the films were of sufficient thickness to perform characterization through grazing angle ATR-FTIR. The FTIR spectrum of the polymer brushes can be found in figure 10.

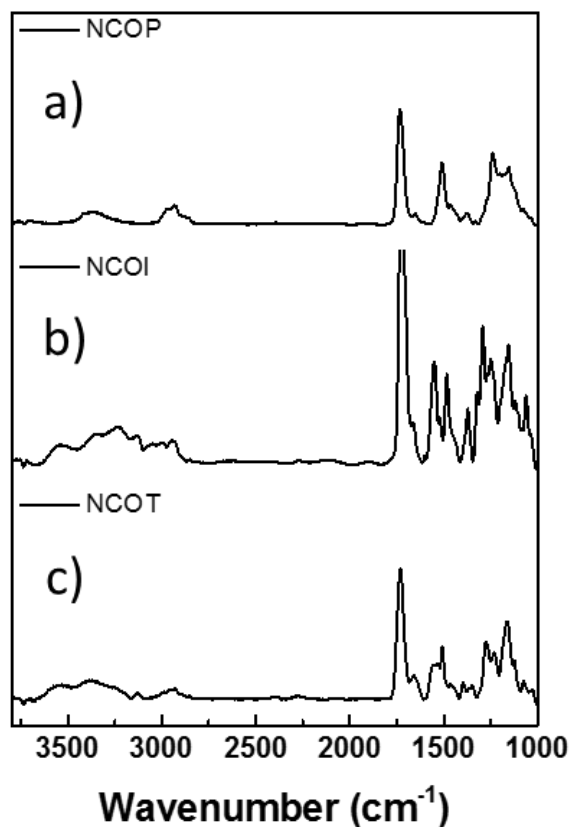


Figure 10 – gATR-FTIR spectrum of pNCOP-, pNCOI- and pNCOT-based polymer brushes. The 3,5-dimethyl pyrazole peak is around 2850 cm^{-1} . The imidazole peak is around 1390 cm^{-1} . The triazole peak is around 1350 cm^{-1} .

Modification of *Poly(2-(1H-1,2,4-triazole-1-carboxamido)ethyl methacrylate)* (pNCOT)

Surface brushes polymerized using triazole-protected isocyanate monomers were modified using various types of thiols. These exchange reactions were carried out at room temperature as described in *Methods 1.5*. The thiols that were used for the exchange were 1-dodecanethiol, benzyl mercaptan, furfuryl mercaptan, 1-thioglycerol and 3-

mercaptopropionic acid. These thiols were chosen for their unique IR signature, as well as a diverse degree of hydrophobicity/hydrophilicity. After the exchange reaction was complete, gATR-FTIR spectroscopy was performed on the surfaces. The resultant IR spectrum can be found in figure 11.

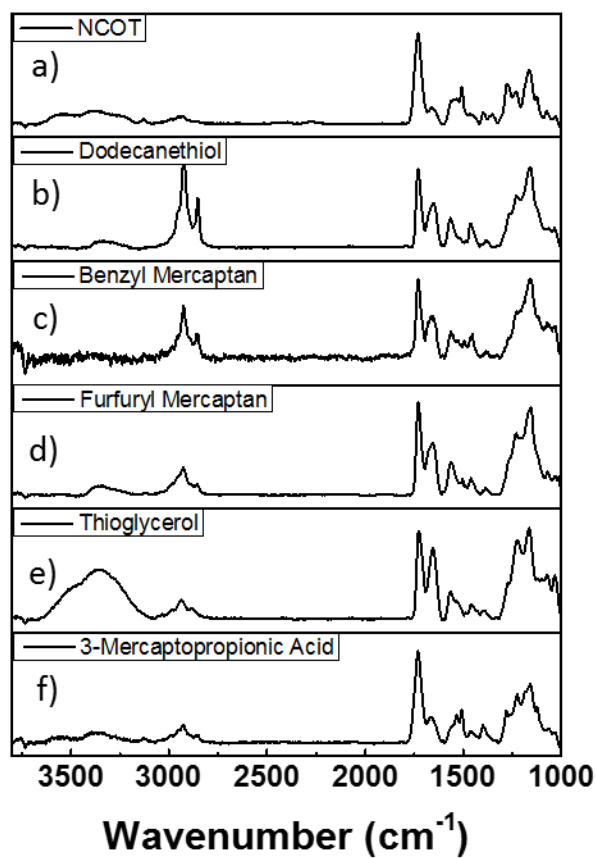


Figure 11 – FTIR spectrum of thiol-modified pNCOT surface brushes using 10b) 1-dodecanethiol, 10c) benzyl mercaptan 10d) furfuryl mercaptan 10e) thioglycerol and 10f) 3-mercaptopropionic acid.

The indicative fingerprints of each thiol can be found in the FTIR spectrum in figure 11. Figure 11a is the silicon wafer with only the polymerized NCOT monomer, and as the exchange reaction proceeds, the triazole peaks disappear and the thiol peaks emerge.

Water contact angle

Substrates modified with NCOI were reacted with 1-dodecanethiol and 1-thioglycerol to demonstrate control of surface properties via room temperature modification of blocked isocyanates via thiol-isocyanate reactions. It was expected that the hydrophobic thiol (1-dodecane thiol) would increase the water contact angle and create a more hydrophobic surface upon reaction. Conversely, 1-thioglycerol was reacted with the blocked isocyanates to create a more hydrophilic surface and therefore decrease the water contact angle. The modifications were monitored by water contact angle and FTIR, which are shown in Figure 12.

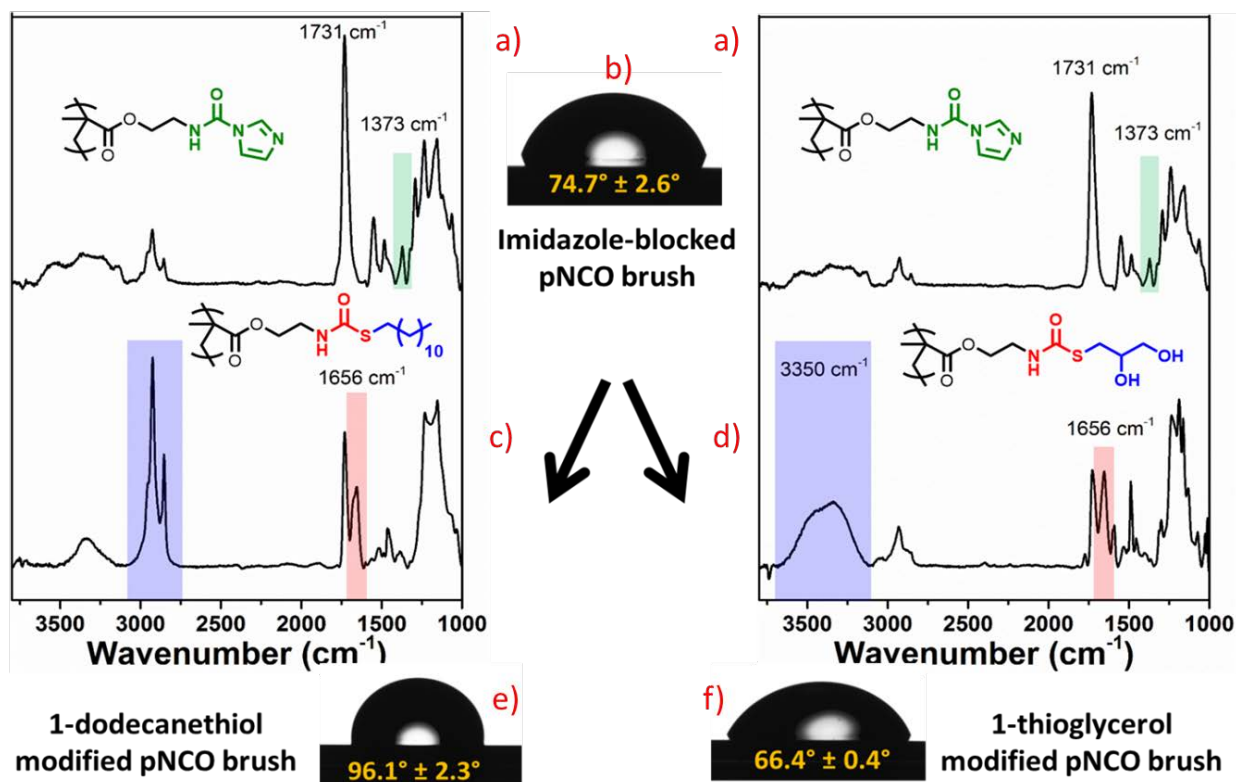


Figure 12 – Water contact angle and FTIR of modified pNCOI brushes with 1-dodecanethiol and 1-thioglycerol. 11a) Polymerized NCOI monomer 11b) water contact angle (WCA) of imidazole-blocked pNCO brush 11c) 1-dodecanethiol modified pNCOI brush 11d) 1-thioglycerol modified pNCOI brush 11e) WCA of 1-dodecanethiol modified pNCOI brush 11f) WCA of 1-thioglycerol modified pNCOI brush.

In Figure 12, it can be seen that the water contact angle of 1-dodecanethiol was increased by approximately 21° , going from 75° to 96° . Also, the appearance of peaks in the IR spectrum in Figure 12a corresponding to the hydrocarbon tail of 1-dodecanethiol can be seen around 2900cm^{-1} . When pNCOI brushes were reacted with 1-thioglycerol, a decrease in water contact angle of approximately 10° was observed. The presence of 1-

thioglycerol was confirmed through FTIR with the appearance in alcohol groups around 3350cm^{-1} .

Thermal regeneration of blocked isocyanates

In addition to deblocking the blocked isocyanates at room temperature via direct nucleophilic displacement, a more traditional thermal regeneration of the isocyanate from its protected form was also explored. It was found that after SIP of the NCOT monomer, the triazole blocking agent could be deprotected at 100°C and *in vacuo*. Silicon substrates that had been modified triazole-blocked polymers and imidazole-blocked polymers were placed modified-side up in a vacuum oven at 100°C and gATR-FTIR spectra (Figure 13) were collected before deblocking and after 18 hours in the vacuum oven. The appearance of a peak at 2275 cm^{-1} corresponding to isocyanate demonstrates that the blocking agents could be successfully removed and the isocyanate functionality restored. The presence of a peak around 1373 cm^{-1} in both IR spectra for the imidazole-blocked brushes indicates that there is remaining blocked imidazole after thermal treatment. This may be a result of the imidazole blocking agents being unable to leave the brush surface due to steric hindrance or that longer times at elevated temperatures in the vacuum oven are needed to remove the blocking agent completely.

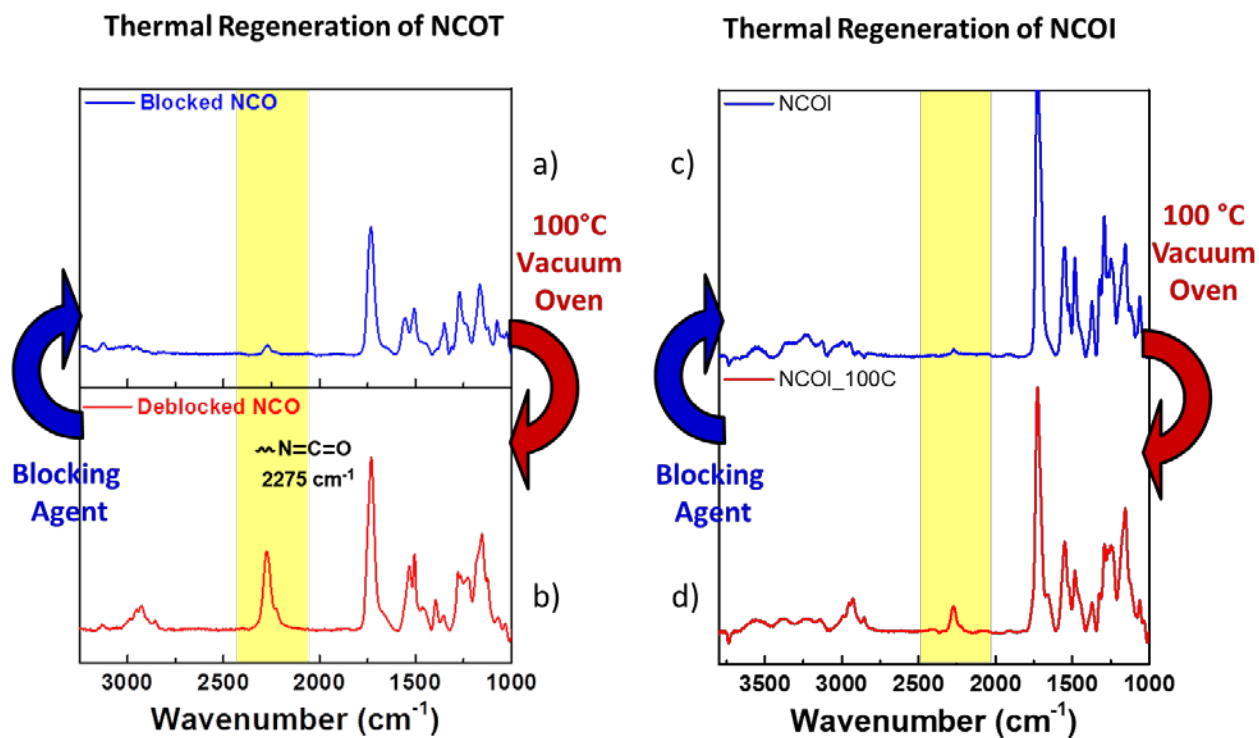


Figure 13 – Thermal regeneration of blocked isocyanates 12a) pNCOT brushes 12b) deprotected pNCOT brushes 12c) pNCOI brushes 12d) deblocked pNCOI brushes.

Chapter V:

Conclusion

The goal of this research project was to synthesize protected isocyanate-functional brushes, and to then determine the kinetic and thermodynamic parameters needed to exchange those blocking agents with thiols. A series of blocked isocyanate methacrylate-based monomers were synthesized successfully and in high yield. Small molecule analogs of the blocked isocyanate monomers were also successfully synthesized and used to determine the conversion of the exchange between blocking agent and thiol, using DBU and, in one case, TEA as catalysts. The model compounds blocked with imidazole and 1,2,4-triazole were found to have a very rapid conversion to thiocarbamate linkages in the presence of DBU. Triazole-model compounds were also found to reach high conversions rapidly using TEA at high mole percentages of catalyst. Blocked isocyanate-functional polymer brushes were successfully synthesized by surface-initiated photopolymerization and characterized by ellipsometry and gATR-FTIR. Once formed, the imidazole and 1,2,4-triazole blocked polymer brushes could then be deblocked through application of vacuum and heat, or by room temperature nucleophilic displacement of the blocking agent with a thiol. Finally, through water contact angle we observed that modification of the blocked isocyanate brushes could change the hydrophobicity or hydrophilicity of the silicon surface, dependent upon the hydrophobicity/hydrophilicity of the thiol modifier.

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